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Publication date:
2014

Document Version
Peer reviewed version

DTU Chemistry
Department of Chemistry

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Introduction

The research interest in biomass conversion to fuels and chemicals has increased significantly in the last decade in view of current problems such as global warming, high oil prices, food crisis and other geopolitical scenarios.

Many different reactions and processes to convert biomass into high-value products and fuels have been proposed in the literature, giving special attention to the conversion of lignocellulosic biomass, which does not compete with food resources and is widely available as a low cost feedstock.

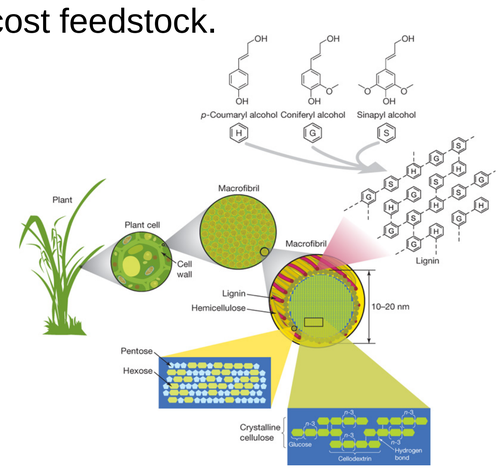


Figure 1. View of the role of lignin, cellulose and hemicellulose in a typical plant.

Lignin constitutes up to 40% of the heating value of lignocellulosic biomass. It is the most complex fraction and is harder to process compared to the sugar fractions.

Linkage type	Softwood lignin Total linkages (%)	Hardwood lignin Total linkages (%)
β-O-4	45-50	60
5-5	19-22	9
β-5	9-12	6
β-1	7-9	7
α-O-4	6-8	-
4-O-5	4-7	6,5
β-β	2-4	3

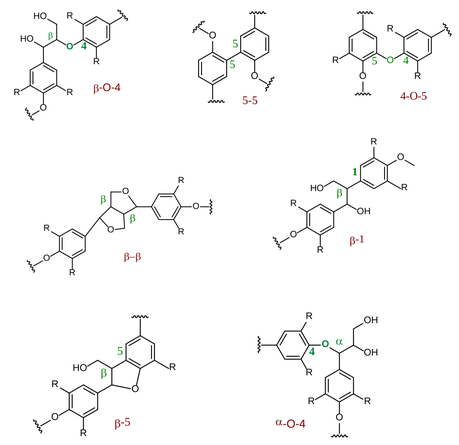


Figure 2. Type of bonds in lignin.

The complexity has led lignin to be treated as a waste stream, and typically burned to produce energy. However, lignin is a significant portion of the total carbon in biomass, and better use of this fraction is a requirement to improve the economic balance of any bio-refinery.
For this reason, research on upgrading lignin has become of recent interest, as many interesting products, mainly aromatics, can potentially be produced from lignin. Here we therefore present an overview conversion of lignin into chemicals using heterogeneous catalysis.

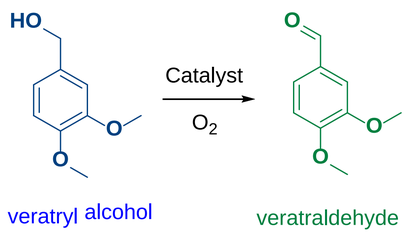
Experimental

Catalyst preparation

An appropriate amount of aqueous solution of ruthenium or manganese precursors was mixed with support (alumina or silica), dried and calcined at 450ºC to get metal the corresponding supported metal oxide catalysts.

Catalytic reactions

A 50 ml autoclave (Microclave reactor from Autoclave Engineers) was charged with an appropriate amount of veratryl alcohol, catalyst (150 mg) and water as solvent (10 ml) and then pressurized with Air (5 bar). The autoclave was heated to 160ºC and the stirring started once the temperature reached 140ºC (300 rpm). After 5 h of stirring, the autoclave was quenched with cold water and analyzed by GC and GC-MS.



Results

Table 1. Data for Veratryl alcohol oxidation with different catalyst.

CATALYST	BET surface AREA (m^2/g)	Veratryl alcohol CONVERSION (%)	Veratraldehyde YIELD (%)
Ru/Al_2O_3	166	93	67
Ru/SiO_2	422	96	46
Mn/Al_2O_3	152	69	17
Al_2O_3	204	46	3
SiO_2	472	59	3
Blank	-	34	2

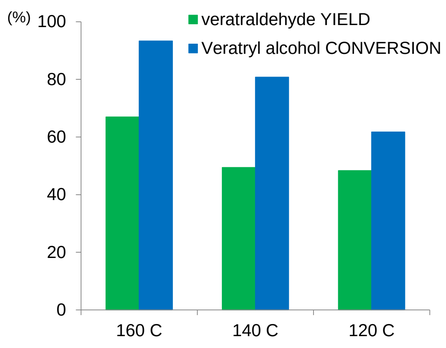


Figure 3. Temperature study on the conversion of veratryl alcohol using Ru/Al_2O_3 as catalyst.

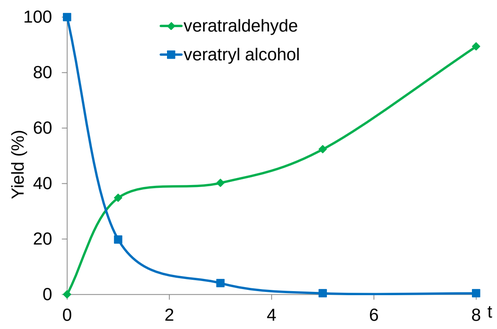


Figure 4. Time-course study on the conversion of veratryl alcohol over Ru/Al_2O_3.

Conclusion

Time-course study revealed that 8 hours of reaction time required to get an optimum yield towards veratraldehyde. Among the catalyst employed, Ru/Al_2O_3 gave a highest yield to veratraldehyde (67 %) along with 93 % conversion of veratryl alcohol. However, Ru/SiO_2 also gave a comparable yield of veratraldehyde. Temperature study shows that 160ºC gives the highest conversion of veratraldehyde over Ru/Al_2O_3.

References

- Chem. Soc. Rev., 41 (2012) 8075
- Energy Fuels, 25 (2011) 4713
- J. Polym. Environ., 10 (2002) 39
- Chem. Rev., 110 (2010) 3552
- J. Catal. 285 (2012) 315
- Chem. Eng. Technol., 34 (2011) 29
- Fuel Process. Technol.45 (1995) 161
- Energy Fuels, 7 (1993) 426
- Chem. Eur. J., 34 (2011) 29
- Eur. Polymer J., 49 (2013) 1151

Acknowledgement

The authors appreciate financial support granted to the International Network Programme (12-132649) from The Danish Agency for Science, Technology and Innovation, Haldor Topsøe A/S and DTU

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Liblice Castle
June 8-11, 2014
Czech Republic

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